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LETTER

How safe are protic ionic liquids? Explosion of pyrrolidinium nitrate

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Sil Wellens,[a,b] Ben Thijs[b] and Koen Binnemans*[a]

A batch of the protic ionic liquid pyrrolidinium nitrate exploded while drying it under reduced pressure at 110 °C, using a rotary evaporator with an oil bath.

Ionic liquids are often considered as safe alternatives for volatile organic solvents, because of their extremely low vapor pressure and their very high flash point.[1] Although ionic liquids can be designed to be energetic materials or even explosives,[2,3] these solvents are in general difficult to ignite. *Protic ionic liquids* (PILs) are a special class of ionic liquids that are formed by the reaction with a nitrogen base and a Brønsted acid.[4] The proton of the Brønsted acid is transferred to the nitrogen atom of the base and an ionic compound is formed, provided that the Brønsted acid is sufficiently strong. A typical example is ethylammonium nitrate (EAN) that is formed by the reaction between ethylamine and nitric acid.[5] Protic ionic liquids are a popular class of ionic liquids because of their easy synthesis and because they are good model systems for physical studies. Several papers on protic ionic liquids have been published in Green Chemistry.[6–9] As part of our ongoing research on the dissolution of metal oxides in ionic liquids,[10] we decided to investigate protic ionic liquids as reactive solvents for metal oxides. A series of different protic ionic liquids was prepared, including pyrrolidinium ionic liquids with different coordinating anions ($[HCOO]^-$, $[HSO_4]^-$, $[NO_3]^-$, $[H_2PO_4]^-$). These pyrrolidinium ionic liquids were first reported by Anouti *et al.*[11] Two different synthetic procedures were described in this reference, one for ionic liquids with organic anions and one for inorganic anions. The difference in the two procedures is primarily the drying step. In the case of ionic liquids with an organic anion, the residual pyrrolidine or acid was evaporated under reduced pressure and the remaining liquid was further dried at 80 °C under reduced pressure (1–5 mmHg). In the case of ionic liquids with inorganic anions, water was removed by addition of 1,2-dichloroethane, followed by azeotropic distillation. After removal of 1,2-dichloroethane, the remaining ionic liquid was dried under vacuum. However, we decided to prepare pyrrolidinium nitrate [Pyrr][NO_3] *via* the method described for the ionic liquids with the organic anions, to avoid the use of carcinogenic 1,2-dichloroethane (Fig. 1). The drying method was slightly modified with respect to the literature method, in the sense that the drying step was performed at 110 °C, instead of 80 °C. The experimental procedure we used was as follows: nitric acid (65% in water) (1 mol, 63.02 g) was added dropwise to pyrrolidine (1 mol, 71.12 g) in a round-bottom flask (250 mL) using a dropping funnel, while being stirred in an ice bath. After stirring at room temperature for 4 hours, the remaining pyrrolidine, water and nitric acid were removed on a rotary evaporator under reduced pressure (16 mbar) at 70 °C. Heating of the flask on the rotary evaporator was done by means of a hot silicon oil bath. Not all of the water could be distilled off, and the temperature was increased stepwise to 110 °C. Suddenly an explosion occurred. The glass round-bottom flask was scattered and part of the hot silicon oil in the heating bath was blasted by the shock to the walls and ceiling in the neighborhood of the rotary evaporator. At the same time, a cloud of reddish-brown nitrogen dioxide gas was visible. Luckily, nobody was injured and there was only material damage.

The explosion can be attributed to the strong oxidizing properties of concentrated nitric acid under the anhydrous conditions, resulting in a violent oxidative decomposition of the organic compounds. A search of the literature revealed that mixing of nitric acid with secondary amines like pyrrolidine has been reported to cause violent reactions. Clark described secondary and tertiary amines as hypergolic with nitric acid.[12]

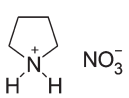

Fig. 1 Structure of the protic ionic liquid pyrrolidinium nitrate.

[a]*KU Leuven, Department of Chemistry, Celestijnenlaan 200F, bus 2404, B-3001 Heverlee, Belgium. E-mail: Koen.Binnemans@chem.kuleuven.be*
[b]*Umicore, Group Research & Development, Competence Area Recycling and Extraction Technologies, Kasteelstraat 7, B-2250 Olen, Belgium*

More recently, Smiglak *et al.* studied the possibility of forming simple energetic ionic liquids *via* the straightforward protonation of heterocyclic amines and they studied the decomposition mechanism by accelerating rate calorimetry (ARC).[13] The authors found that 1-methylimidazolium nitrate, obtained by mixing of 1-methylimidazole with nitric acid, is a very energetic material. Ethylammonium nitrate has been claimed to be a liquid monopropellant.[14] On the other hand, non-protic ionic liquids with nitrate anions are much less reactive. Schneider *et al.* found no noticeable reactivity of these ionic liquids towards fuming nitric acid.[15]

This incident shows that drying of nitrate protic ionic liquids can be very hazardous. This is important to realize, given the popularity of protic ionic liquids such as ethylammonium nitrate. It is recommended not to heat these ionic liquids above 80 °C, but one has to be aware of the fact that there could be safety issues with protic nitrate ionic liquids even at lower temperatures. Vacuum freeze-drying is suggested as a safer alternative to heating in a vacuum for drying of these protic ionic liquids.[16]

Although many studies have been devoted in the recent years to the toxicity of ionic liquids, the chemical hazards of these solvents are still much less investigated.[17,18] We hope that this letter to the Editor will lead to an increased awareness of the potential dangers of heating protic nitrate ionic liquids.

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